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Revisiting the S-Au(111) interaction: Static or dynamic?

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The chemical inertness typically observed for Au does not imply a general inability to form stable bonds with non-metals but is rather a consequence of high reaction barriers.¹ The Au-S interaction is probably the most intensively studied interaction of Au surfaces with non-metals as, for example, it plays an important role in Au ore formation,² and controls the structure and dynamics of thiol-based self-assembled-monolayers (SAMs).³⁻⁵ In recent years a quite complex picture of the interaction of sulfur with Au(111) surfaces emerged, and a variety of S-induced surface structures was reported under different conditions. The majority of these structures were interpreted in terms of a static Au surface, where the positions of the Au atoms remain essentially unperturbed. Here we demonstrate that the Au(111) surface exhibits a very dynamic character upon interaction with adsorbed sulfur: low sulfur coverages modify the surface stress of the Au surface leading to lateral expansion of the surface layer; large-scale surface restructuring and incorporation of Au atoms into a growing two-dimensional AuS phase were observed with increasing sulfur coverage. These results provide new insight into the Au-S surface chemistry, and reveal the dynamic character of the Au(111) surface.

Gold is considered to be the most noble of all metals. Traditionally gold is widely used in jewellery, however, due its unique blend of properties gold also becomes an increasingly important material in industrial applications. For example, the high electronic conductivity in combination with corrosion resistance makes gold-plated contacts an essential part in microelectronics. Due to its chemical inertness gold is also an attractive substrate for surface science studies, for instance gold films are widely used as substrate for alkanethiol-based self-assembled monolayers (SAMs).³⁻⁵ On the other hand, it is much less known that gold can exhibit very interesting catalytic properties, and indeed gold-based catalysts are being developed for industrial oxidation processes.^{6,7}

In the present work we focus on the dynamics of the Au surface as affected by the Au-S interaction, which is one of the most relevant Au-non-metal interactions.

Real-time scanning tunnelling microscopy (STM) was employed to directly monitor mass-transport involved in Au-S surface interaction. Specifically, we address the nature of the S-induced rectangular surface features on Au(111), which were observed under a wide variety of experimental conditions⁸⁻¹² and predominantly attributed to the formation of S₈ molecules adsorbed on the surface. In contrast, our experiments provide strong evidence that these rectangular structures arise from the formation of a 2D AuS phase which involves a dynamic rearrangement of the surface landscape and large scale mass transport.

The clean Au(111) surface exhibits a characteristic “herringbone” reconstruction pattern that is caused by the presence of tensile surface stress. This tensile stress drives the incorporation of an additional 4% of Au atoms in the surface layer leading to a uniaxial contraction along the close-packed <110> directions.^{13,14} The resulting fcc and hcp stacking regions are separated by rows of bridging Au atoms which appear as ridges in STM images. A regular arrangement of rotational domains of uniaxially contracted areas allows for a more isotropic stress distribution and gives rise to the observation of the characteristic herringbone pattern of the clean Au(111) surface (fig 1a).

The surface stress of the clean Au(111) surface is strongly modified by the interaction with adsorbed sulfur atoms, which leads to a relaxation of the surface layer in the low coverage regime, and the formation of a two-dimensional AuS phase at higher coverage. The relaxation of the stress-induced reconstruction of the clean Au(111) surface with increasing sulfur coverage was monitored by real-time STM (Fig. 1). Our experiments reveal that sulfur coverages as low as 0.05 ML significantly modify the reconstruction pattern of the clean surface even at room temperature. The sulphur coverage is determined using Auger electron spectroscopy (AES). According to a simple model proposed by Ibach,¹⁵ such an adsorbate-induced modification of the surface stress can qualitatively be explained by charge being transferred from the bonds between the substrate surface atoms to the adsorbate atoms, thereby creating compressive surface stress. The appearance of serrated step edges upon sulfur adsorption indicates that the compressive stress is high enough to drive the ejection of Au atoms, which in turn agglomerate at ascending step edges; diffusion across descending steps at room temperature is hindered by the existence of a Schwoebel barrier. The experimentally

observed change in the step edge position during sulphur adsorption is consistent with the amount of Au expected based on the amount of excess Au in the reconstruction (4%).

It is quite remarkable that a sulfur coverage of only 0.1 ML is sufficient to completely lift the herringbone reconstruction at room temperature and thus drives a lateral expansion of the Au surface layer by 4%. The expansion/contraction of nanoporous metals in response to modification of the charge density in the surface layer has recently attracted much interest due to potential actuator and sensor applications.¹⁶⁻¹⁸ In this case, the modification of the charge density was achieved by applying an external electrical field rather than by an adsorbate as in the present study.

The unreconstructed Au(111) surface is stable up to a sulfur coverage of 0.3 ML where sulfur forms an ordered ($\sqrt{3}\times\sqrt{3}$)R30° adlayer, as verified by LEED (adsorbed S is too mobile to be imaged by STM). Above this coverage we observe a dynamic rearrangement of the Au surface caused by formation of a 2D AuS overlayer phase (figure 2). The nucleation of small irregularly shaped islands is accompanied by the formation of monoatomic etch pits, finally leading to a sponge-like surface morphology with a sulfur saturation coverage of 0.6 ML. These observations reveal massive mass transport: Au atoms are removed from the surface layer, thereby creating pits, and incorporated into the growing AuS islands.

The appearance of etch pits suggests that S continues to weaken the Au-Au bonds with increasing S coverage, finally reaching a point where the energy necessary to remove Au atoms from the surface layer is overcompensated by the energy released by the formation of mobile Au-S species. This indicates that the Au-S bond must be relatively strong, at least strong enough to compensate the energy costs accompanied by the removal of Au atoms from regular surface lattice sites. Indeed, stable gold sulfide clusters (Au₂S)_n, n = 1, 2, have been identified by *ab initio* calculations.¹⁹ It is interesting that a preferred etching of Au step-edge atoms is *not* observed. The mobilization of Au surface atoms by the interaction with sulfur or sulfur-containing molecules seems to be a general phenomenon: For example, the formation of vacancies and etch pits has also been observed during the preparation of alkanethiol-based SAMs on Au(111),^{3,4,20,21} as well as during the interaction of cysteine with Au(110).²²

Significant changes in the surface morphology are observed during annealing at 450 K: the sponge-like AuS phase formed at room temperature is transformed into an ordered two-dimensional AuS overlayer which produces a very complex, but well-defined LEED pattern (figure 3). Simultaneously large Au vacancy islands of monoatomic depth develop by Ostwald ripening of the irregular etch pits created during formation of the AuS phase at 300 K. Both terraces and vacancy islands are uniformly covered by the 2D AuS phase based on high-resolution STM images.

The AuS overlayer exhibits a 1:1 stoichiometry: AES indicates a sulfur coverage of 0.5 ML, i.e. the sulfur coverage decreases by ~20% during annealing, in excellent agreement with the results obtained by a radioactive ³⁵S tracer-technique;^{23,24} the number of Au

atoms incorporated in the 2D AuS phase was estimated to be 0.5 ML by determining the surface area covered by vacancy islands.

High-resolution STM images of the ordered 2D AuS phase reveal a quasi-rectangular unit cell, with lattice parameters of $(8.8 \text{ \AA} \pm 0.4) \times (8.2 \pm 0.4) \text{ \AA}^2$ and $82^\circ \pm 4^\circ$ (Figure 3b, insert). This seems to be a favourable surface structure under a wide variety of experimental conditions. For example, very similar sulfur-induced surface structures on Au(111) were observed by STM after treatment with aqueous solutions of Na_2S or H_2S .⁸⁻¹² The interpretation of these rectangular surface features is controversial although a model of adsorbed S_8 molecules was preferred by the majority of authors. However, the mobilization and incorporation of Au atoms into the growing 2D sulfide phase as revealed by our STM experiments clearly rules out the simple sulfur adlayer model. The complex LEED pattern shown in Figure 3a is consistent with the STM results and can be interpreted in terms of an incommensurate AuS phase with a quasi-rectangular unit cell. Interestingly, an early study reported a similar LEED pattern from Au(111) surfaces treated with $\text{H}_2\text{S}/\text{H}_2$ gas mixtures at elevated temperatures.^{23,24}

Our results thus suggest a new picture of the S-Au(111) interaction: S-induced perturbation of the Au surface charge density causes a stress relaxation at low S-coverages and a dynamic restructuring of the surface landscape during formation of a 2D AuS at higher coverages. The incorporation of stoichiometric amounts of metal atoms in adsorbate-induced surface structures is not unique to the S/Au(111) interaction but has also been observed for a variety of other systems, such as S/Ni(111)²⁵, O/Ag(110) and O/Cu(110).²⁶ In the latter two cases, however, the metal atoms (Ag, Cu respectively) appear to be supplied from the energetically less favourable step edge sites. In general, adsorbate-induced mass transport and formation of stoichiometric metal-adsorbate surface structures requires that the metal adsorbate interaction is strong enough to compensate the energy cost of removing metal atoms from regular lattice sites. Thus the AuS formation observed in the present study directly reflects the strength of the Au-S interaction.

The observed phenomena provide a basis for potential sensor or actuator applications: In materials with a high surface-to-volume ratio, such as nanoporous gold, the large S-induced expansion of the Au surface layer (4%) should lead to macroscopically observable dimension changes. Another interesting outlook is the synthesis of single-layer transition-metal disulfide structures using the 2D AuS phase as a sulphur reservoir. Using this approach, we recently demonstrated the preparation of single-layer MoS_2 and TiS_2 structures on Au(111).^{27,28} Transition metal dichalcogenides are very promising candidates for high mobility flexible inorganic FETs.²⁹

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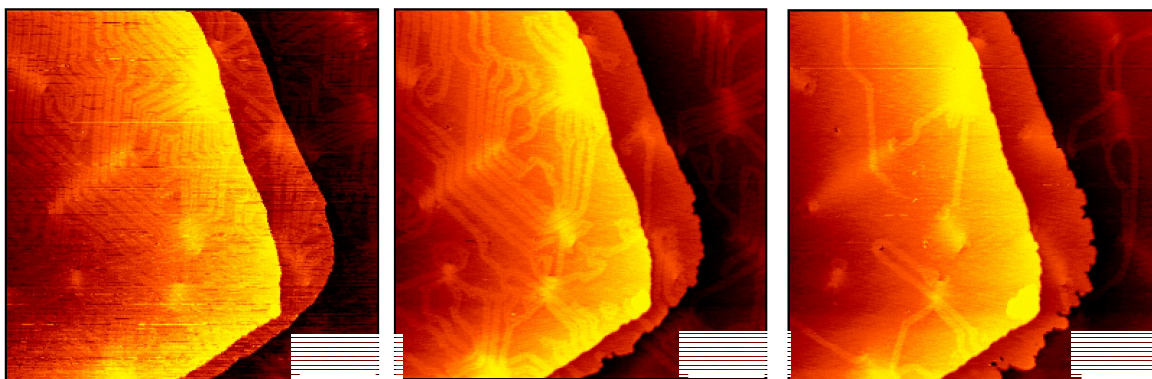


Figure. 1:

Sulfur-induced modification of the Au herringbone reconstruction illustrated by constant-current STM images. (A) Typical herringbone reconstruction pattern of the clean Au(111) surface caused by uni-axial compression of the surface layer by 4%. Note that the elbow sites of the herringbone reconstruction are preferentially aligned along defects (partial Shockley dislocations) that appear as bright spots in the image. (B) A sulfur coverage of 0.05 ML is sufficient to partially lift the herringbone reconstruction. This indicates that adsorbed sulfur atoms decrease the charge density between Au surface atoms thereby turning the tensile surface stress of the clean Au surface into a compressive surface stress. This drives the ejection of Au atoms, which agglomerate at ascending steps as indicated by the appearance of serrated step edges. (C) Lifting of the reconstruction is almost complete reaching a S coverage of 0.1 ML, and corresponds to a lateral expansion of the Au surface layer by 4%. Note the increased serration of the step edges.

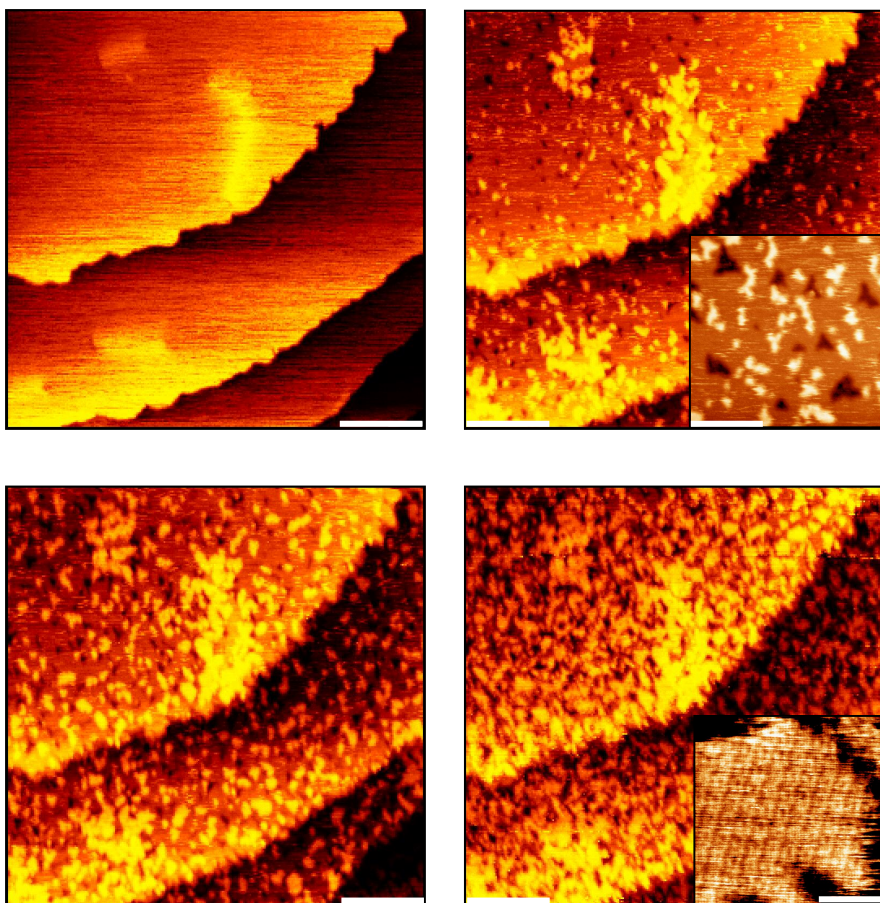


Figure 2:

Dynamics of the formation of a 2D AuS overlayer captured by real-time STM during continuous SO_2 exposure at room temperature. (A) unreconstructed Au(111) surface with a sulfur coverage of 0.3 ML. The sulfur forms an ordered $(\sqrt{3}\times\sqrt{3})R30^\circ$ adlayer as observed by LEED. This adlayer is not observable by STM. (B) Early stage of S-induced corrosion/etching of the Au(111) surface. Dark areas (emphasized in the close-up) correspond to monoatomic etch pits. Simultaneously small AuS clusters nucleate on terraces, preferentially at defect sites. (C) The number of both pits and AuS clusters increases with increasing S-coverage. (D) The reaction is completed once the S coverage reaches a value of 0.6 ML. At this point the surface is covered with a sponge-like gold sulfide overlayer exhibiting short-range order as demonstrated by the inset.

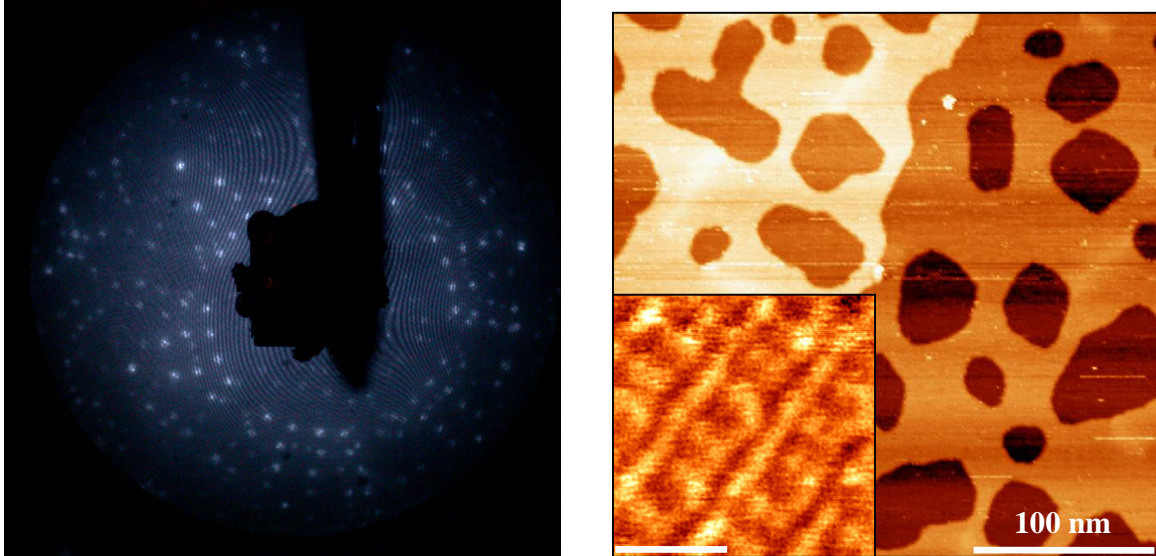


Figure 3:

A well ordered 2D-AuS phase develops during annealing to 450 K. (A) The structure exhibits a very complex LEED pattern which can be explained by an incommensurate structure with a nearly quadratic unit cell. (B) STM reveals the formation of large vacancy islands by Oswald ripening which cover about 50% of the surface, thus indicating the incorporation of 0.5 ML of Au atoms into the 2D AuS phase. The 2D AuS phase exhibits a quasi-rectangular structure (inset), and uniformly covers both vacancy islands and terrace areas.

Methods:

All experiments were performed in an ultrahigh vacuum (UHV) system with a base pressure of 4×10^{-10} torr. The system is equipped with a home-made “beetle-type” Scanning Tunneling Microscope (STM) and commercial instrumentation for Auger Electron Spectroscopy (AES) and Low energy Electron Diffraction (LEED). The sample was radiatively heated via a tungsten filament located behind the sample. The temperature was monitored by a chromel/alumel thermocouple affixed to the sample holder. The Au sample was cleaned by cycles of Ar^+ sputtering (1000 eV, $\sim 5 \mu\text{A}$) at 300 K, followed by annealing to 700 K for 10 minutes and 600 K for 60 minutes. Following this procedure, the characteristic $\text{Au}(111)-(22 \times \sqrt{3})$ “herringbone” reconstruction was observed by LEED and STM. The Au sample used for these experiments exhibits many surface defects, most likely partial Shockley dislocations³⁰ introduced by the gentle annealing procedures used in the present study.

SO_2 (“Matheson”, anhydrous grade) served as a source of sulfur, and was introduced by chamber backfilling. Only a small fraction of the admitted SO_2 molecules decomposes on the $\text{Au}(111)$ surface and deposits sulfur. The sulfur coverage was monitored by AES and calibrated relative to the S induced $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ LEED pattern corresponding to a S coverage of ~ 0.3 ML. At any point of the experiment, sulfur is the only species on the surface detected by AES. The oxygen released by SO_2 decomposition seems to be removed via an abstraction reaction with excess SO_2 ³¹. In order to rule out effects due to electron-induced reactions, the experiments were reproduced with the ion gauge turned off.

All STM images shown in this work were collected at room temperature using $\text{Pt}_{0.8}\text{Ir}_{0.2}$ tips. The STM scanner was calibrated against the unit cell of the $\text{Au}(111)$ surface.

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